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(54) **LITHIUM SECONDARY BATTERY**

(57)Abstract:
PURPOSE: To provide a lithium secondary battery with excellent charge/discharge cycle characteristics.
CONSTITUTION: A negative electrode is formed by pressing slurry or paste containing an active material capable of electrochemically absorbing or releasing lithium ions, a binder, and a required conductor against a coil-shaped, film- shaped, or plate-shaped current collector to form an active material layer, and a lithium secondary battery uses the negative electrode in which hardness of the active material is lower than hardness of the current collector. The active material layer contains additive powder having higher hardness than the current collector. Adhesion between the active material layer and the current collector in the negative electrode is increased, and the active material in the negative electrode hardly separates from the current collector in charge/ discharge cycles.

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CLAIMS

[Claim]
[Claim 1] Electrochemically a lithium ion An occlusion and the active material which can be emitted, The slurry or paste containing a binding agent and a required electric conduction agent The shape of a foil, In a lithium secondary battery equipped with the negative electrode with the degree of hardness of the aforementioned active material lower than the degree of hardness of the aforementioned collection **** which is a negative electrode in which it was stuck by pressure on the shape of a film, and tabular ******, and the active material layer was formed The lithium secondary battery with which the aforementioned active material layer is characterized by containing the additive powder with a degree of hardness higher than the aforementioned collection ****.
[Claim 2] The lithium secondary battery of the claim 1 publication whose aforementioned collection **** is copper.

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DETAILED DESCRIPTION

[Detailed description]
[0001]
[Field of the Invention] this invention relates to a lithium secondary battery. in detail a lithium ion electrochemically An occlusion and the active material which can be emitted, The slurry or paste containing a binding agent and a required electric conduction agent The shape of a foil, It is related with enhancement of the adhesion of the active material layer of a negative electrode and ****** aiming at improving the charge-and-discharge cycle property of a lithium secondary battery equipped with the negative electrode with the degree of hardness of an active material lower than the degree of hardness of ****** which is a negative electrode in which it was stuck by pressure on the shape of a film, and tabular ******, and the active material layer was formed. In addition, although it is a lithium if the active material of the negative electrode of a lithium secondary battery understands this in a narrow sense, suppose that this is understood in a wide sense and an occlusion, the graphite to emit include a lithium ion in an active material electrochemically on these specifications.
[0002]
[A Prior art and Object of the Invention] When a lithium secondary battery selects a positive-electrode material suitably in recent years, from high-capacity-izing being possible, it is observed and various metallic oxides are proposed as a positive-electrode material for high-capacity-izing. For example, $LiCoO_2$ already used The $LiCoO_2$ which is one and has the electric discharge capacity more than 120mAh/g It is easily obtained by the solid phase technique.
[0003] However, the charge-and-discharge cycle property of the lithium secondary battery which used a certain kind of negative electrode is not yet enough practically so that it may state below.
[0004] That is, the negative electrode of a lithium secondary battery is produced by rolling out with a roller and generally, forming an active material layer on the shape of a foil, the shape of a film, and tabular ******, after applying or ****ing a slurry or a paste (negative electrode mixture). However, since this kind of negative electrode does not have the good adhesion of an active material layer and ******, an active material tends to drop out of a negative electrode. This phenomenon is especially remarkable when the graphite which is elasticity is used as an active material compared with ******, and for this reason, the badness of the charge-and-discharge cycle property of this kind of lithium secondary battery was pointed out.
[0005] this invention is made that the problem which this kind of specific lithium secondary battery holds should be solved, and the place made into the purpose is by raising the adhesion of an active material layer and ****** to offer the lithium secondary battery which has the outstanding charge-and-discharge cycle property.
[0006]
[The means for solving a technical problem] The lithium secondary battery (this invention cell) concerning this invention for attaining the above-mentioned purpose Electrochemically a lithium ion An occlusion and the active material which can be emitted, The slurry or paste containing a binding agent and a required electric conduction agent The shape of a foil, In a lithium secondary battery equipped with the negative electrode with the degree of hardness of the aforementioned active material lower than the degree of hardness of the aforementioned collection **** which is a negative electrode in which it was stuck by pressure on the shape of a film, and tabular ******, and the active material layer was formed The aforementioned active material layer is characterized by containing the additive powder with a degree of hardness higher than the aforementioned collection ****.
[0007] As additive powder, alumina (aluminum2 O3) powder, diamond powder, ****-ized boron (BN) powder, boron-carbide (B_4C) powder, and titanium-carbide (TiC) powder are illustrated. In addition, in order that additive powder may increase the touch area of an active material layer and ****** and may prevent the defluxion from ****** of an active material, an active material layer is made to contain.
[0008] The amount of additive powder has desirable 0.01 - 1 weight section to the AUW 100 weight section of an active material, a binding agent, and a required electric conduction agent, and its 0.05 - 1 weight section is more desirable. It becomes impossible to fully improve a charge-and-discharge cycle property, in order that the adhesion of an active material layer and ****** may not improve so much, if there are few amounts of additive powder than 0.01 weight section. On the other hand, if there are more amounts of additive powder than 1 weight section, the enhancement effect in adhesion according to increase in quantity is not not only acquired, but a unit mass and the negative-electrode capacity per unit volume will fall.
[0009] Since there is meaning which applies this invention if a degree of hardness is lower than ****** although lithium alloys (a lithium-aluminium alloy, a lithium-lead alloy, lithium-tin alloy, etc.) and carbon materials (a graphite, corks, organic

teaches away from 71

substance baking field, etc.) can be electrochemically mentioned for a lithium ion as an example of an occlusion and the active material which can be emitted, it is not limited to especially these.

[0010] this invention relates to enhancement of a negative electrode. Therefore, about other components which constitute cells, such as a positive electrode, nonaqueous electrolyte, and a separator, the various things currently used [which are used and are former-proposed] as an object for lithium secondary batteries can be used.

[0011] For example, as a positive active material, they are TiS2, MoS2, and NbSe3. Metal chalcogen ghost;Cr2 O5 of a grade, and V2 O5 The lithium (a kind of transition element [as which M was chosen out of Co, nickel, V Fe, and Mn / at least], 0< x<=1.3, 1.8<=z<=2.2)-transition-metals multiple oxide of metallic-oxide [of a grade];, Lix MOz, etc. can be used.

[0012] Moreover, as nonaqueous electrolyte, they are LiPF6 and LiBF4 to the mixed solvent of high dielectric constant solvents, such as ethylene carbonate, vinylene carbonate, and propylene carbonate, or these high dielectric constant solvents, and low boiling point solvents, such as diethyl carbonate, dimethyl carbonate, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, and ethoxy methoxyethane. What melted the solute of a grade can be used. In addition, a solid electrolyte or a gel-like electrolyte (false solid electrolyte) can also be used outside a liquid electrolyte.

[0013]

[Operation] Since the degree of hardness was higher than ******, the additive powder contained in the active material layer by which the slurry or the paste was stuck [by pressure] and formed on ****** will be caved in by the part into ******, and the touch area of an active material layer and ****** increases. Consequently, since the adhesion of an active material layer and ****** improves, an active material comes to seldom drop out of ******.

[0014]

[Example] It is possible to change this invention suitably in the domain which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is explained still in detail based on an example.

[0015] (Examples 1-6)

LiNiO2 as a [production of positive electrode] active material Acetylene black as an electric conduction agent, A mixture is prepared. the polyvinylidene fluoride as a binding agent -- the weight ratio 95:2:3 -- mixing -- a positive electrode -- this positive electrode -- after made the N-methyl-2-pyrrolidone distribute a mixture, having prepared the slurry, having applied this slurry on the aluminum foil, having rolled it out and piercing with a diameter of 20mm in the shape of a disk, it heat-treated by 150 degreeC for 2 hours, and the positive electrode was produced

[0016] The graphite as a [production of negative electrode] active material, and the polyvinylidene fluoride as a binding agent, aluminum2 O3 (Mohs hardness 9) of 3 micrometers of the mean particle diameters as additive powder A mixture is prepared. the weight ratio 95:5:0.01, 95:5:0.05, 95:5:1, 95:5:10 and 95:5:20, or 95:5:30 -- mixing -- a negative electrode -- each negative electrode -- a mixture is distributed to an N-methyl-2-pyrrolidone -- making -- a slurry -- preparing -- these slurries -- each -- after having applied on the copper foil (Mohs hardness 3) as collection ****, having rolled out and piercing with a diameter of 20mm in the shape of a disk, it heat-treated by 150 degreeC for 2 hours, and six sorts of negative electrodes were produced In addition, the negative-electrode active material layer thickness was set to 150 micrometers (also in the following examples and examples of a comparison, the negative-electrode active material layer of the same thickness was formed). 3 um

[0017] The lithium perchlorate (LiClO4) was melted at a rate of 1M (a mol/liter) to the mixed solvent of the volume ratio 1:1 of [manufacture of nonaqueous electrolyte] propylene carbonate, and 1 and 2-dimethoxyethane, and nonaqueous electrolyte was prepared to it.

[0018] this invention cells A1-A6 (flat type lithium secondary battery) were assembled using the positive electrode, the negative electrode (six sorts of negative electrodes), and nonaqueous electrolyte beyond [assembly of a cell] (3.0mm in the cell dimension:diameter of 24.0mm, thickness). In addition, the fine porosity layer made from polypropylene was used, and this was made to impregnate previous nonaqueous electrolyte as a separator.

[0019] (Example 7) the weight ratio of a graphite, a polyvinylidene fluoride, and the diamond powder (Mohs hardness 10) of 3 micrometers of mean particle diameters -- the negative electrode of 95:5:1 -- a mixture -- this invention cell A7 was assembled like examples 1-6 except having used it in production of a negative electrode

[0020] (Example 8) the weight ratio of a graphite, a polyvinylidene fluoride, and ****-ized boron (it checked that Mohs hardness 4.5 was above from the comparison with iron) -- the negative electrode of 95:5:1 -- this invention cell A8 was assembled like examples 1-6 except having used the mixture in production of a negative electrode

[0021] (Example 9) the weight ratio of a graphite, a polyvinylidene fluoride, and a boron carbide (it checked that Mohs hardness was 4.5 or more from the comparison with iron) -- the negative electrode of 95:5:1 -- this invention cell A9 was assembled like examples 1-6 except having used the mixture in production of a negative electrode

[0022] (Example 10) the weight ratio of a graphite, a polyvinylidene fluoride, and a titanium carbide (it checked that Mohs hardness was 4.5 or more from the comparison with iron) -- the negative electrode of 95:5:1 -- this invention cell A10 was assembled like examples 1-6 except having used the mixture in production of a negative electrode

[0023] (Example of a comparison) the weight ratio of a graphite and a polyvinylidene fluoride -- the negative electrode of 95:5:1 -- comparison cell B was assembled like examples 1-6 except having used the mixture in production of a negative electrode

[0024] About [charge-and-discharge cycle examination] each cell, after charging to 4.3V by 1mA, the charge-and-discharge cycle examination which makes 1 cycle the process which discharges to 2.0V by 3mA was performed, and it asked for the capacity maintenance factor [capacity maintenance-factor (%) =(electric discharge capacity of electric discharge capacity / 1 cycle scale division of 100 cycle scale division) x100] of 100 cycle scale division. A result is shown in Table 1.

CAPACITY MAINTENANCE FACTOR (100 cycles / 1 cycle)

[0025]

[Table 1]

電池	正極の活物質	負極の活物質	添加剤粉末	添加剤粉末の負極への添加量（重量部）	100サイクル目の容量維持率（%）
A1	$LiNiO_2$	黒鉛	Al_2O_3 粉	0.01	90
A2	$LiNiO_2$	黒鉛	Al_2O_3 粉	0.05	95
A3	$LiNiO_2$	黒鉛	Al_2O_3 粉	1	95
A4	$LiNiO_2$	黒鉛	Al_2O_3 粉	10	95
A5	$LiNiO_2$	黒鉛	Al_2O_3 粉	20	95
A6	$LiNiO_2$	黒鉛	Al_2O_3 粉	80	95
A7	$LiNiO_2$	黒鉛	ﾀﾞｲﾔﾓﾝﾄﾞ粉	1	95
A8	$LiNiO_2$	黒鉛	BN粉	1	96
A9	$LiNiO_2$	黒鉛	B_4C 粉	1	97
A10	$LiNiO_2$	黒鉛	TiC 粉	1	96
B	$LiNiO_2$	黒鉛	—	—	80

WITHIN NOW CLAIMED RANGE

indicates that 30% ~~retention~~ inclusion has good characteristics

[0026] As shown in Table 1, this invention cells A1-A10 have a high capacity maintenance factor compared with comparison cell B. From this, by making the active material layer of a negative electrode contain the additive powder with a degree of hardness higher than ****** shows that a charge-and-discharge cycle property can improve the charge-and-discharge cycle property of the conventional lithium secondary battery (comparison cell B is equivalent to this) which was not good, in order that an active material may tend to drop out of ******.

[0027]

[Effect of the invention] Since the adhesion of the active material layer and ****** in a negative electrode is good, the active material of a negative electrode seldom drops out of ****** at the time of a charge-and-discharge cycle. For this reason, this invention cell is excellent in a charge-and-discharge cycle property.

[Translation done.]

identifies cells of invention as A1-A10!

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SECONDARY LITHIUM BATTERY

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Claims

1. A secondary lithium battery, characterized by the fact that in a secondary lithium battery equipped with a negative electrode in which an active material layer is formed by pressing a slurry or paste containing an active material which can electrochemically occlude and discharge lithium ions, a binder, and a necessary electric conductor on a foil-shaped, film-shaped, or sheet-shaped current collector and the hardness of the above-mentioned active material is lower than the hardness of the above-mentioned current collector, the above-mentioned active material layer includes an additive powder with a hardness higher than that of the above-mentioned current collector.

2. The secondary lithium battery of Claim 1, characterized by the fact that the above-mentioned current collector is made of copper.

Detailed explanation of the invention

[0001]

[1] Numbers in the margin indicate pagination in the foreign text.

(Industrial application field)

The present invention pertains to a secondary lithium battery. More specifically, the present invention pertains to an improvement of the adhesion of an active material layer of a negative electrode and a current collector in order to improve the charge and discharge cycle characteristics of a secondary lithium battery equipped with a negative electrode in which an active material layer is formed by pressing a slurry or paste containing the active material which can electrochemically occlude and discharge lithium ions, a binder, and a necessary electric conductor on a foil-shaped, film-shaped, or sheet-shaped current collector and the hardness of the active material is lower than the hardness of the current collector. Also, the active material of the negative electrode of the secondary lithium battery is lithium in a narrow sense, however in this specification, in a broad sense, graphite, etc., which only electrochemically occlude and discharge lithium ions are also included.

[0002]

(Prior art and problems to be solved by the invention)

Recently, since the capacity of the secondary lithium battery can be increased by appropriately selecting a positive electrode material, it has been highlighted, and as the positive

electrode material for the increase of the capacity, various metal oxides are proposed. For example, $LiCoO_2$ which has already been practically used is one of them, and $LiCoO_2$ with a discharge capacity of 120 mAh/g or more is easily obtained by a solid-phase method.

[0003] However, the charge and discharge cycle characteristics of a secondary lithium battery using a certain kind of negative electrode is not practically sufficient, yet, as mentioned below.

[0004] In other words, the negative electrode of the secondary lithium battery is generally manufactured by spreading or installing a slurry or paste (negative electrode mixture) on a foil-shaped, film-shaped, or sheet-shaped current collector and forming an active material layer by rolling it by a roller. However, in this kind of negative electrode, since the adhesion of the active material layer and the current collector is not good, the active material is easily dropped from the negative electrode. This phenomenon is distinct especially in the case where graphite, etc., softer than the current collector are used as the active material. For this reason, the inferiority of the charge and discharge cycle characteristics of this kind of secondary lithium battery has been indicated.

[0005] The present invention solves the problems of such a specific secondary lithium battery, and its purpose is to provide a secondary lithium battery with excellent charge and discharge cycle characteristics by improving the adhesion of an active material layer and a current collector.

[0006]

(Means to solve the problems)

In order to achieve the above-mentioned purpose, the secondary lithium battery of the present invention (the battery of the present invention) is characterized by the fact that in a secondary lithium battery equipped with a negative electrode in which an active material layer is formed by pressing a slurry or paste containing an active material which can electrochemically occlude and discharge lithium ions, a binder, and a necessary electric conductor on a foil-shaped, film-shaped, or sheet-shaped current collector and the hardness of the above-mentioned active material is lower than the hardness of the above-mentioned current collector, the above-mentioned active material layer includes an additive powder with a hardness higher than that of the above-mentioned current collector.

[0007] As the additive powder, alumina (Al_2O_3) powder, diamond powder, boron nitride (BN) powder, boron carbide (B_4C) powder, and titanium carbide (TiC) powder are mentioned. Also, the

additive powder is included in the active material layer to prevent the drop of the active material from the current collector by increasing the contact are of the active material layer and the current collector.

[0008] The amount of additive powder is preferably 0.01-1 part by weight, more preferably 0.05-1 part by weight to the total weight of active material, binder, and necessary electric conductor at 100 parts by weight. If the amount of additive powder is smaller than 0.01 part by weight, since the adhesion of the active material layer and the current collector is not considerably improved, the charge and discharge cycle characteristics cannot be sufficiently improved. On the other hand, if the amount of additive powder is larger than 1 part by weight, not only the adhesion improvement effect in accordance with the increase of the amount cannot be obtained, but the negative electrode capacity per unit mass and unit volume is lowered.

[0009] As detailed examples of the active material that can electrochemically occlude and discharge the lithium ions, lithium alloys (lithium-aluminum alloy, lithium-lead alloy, lithium-tin alloy, etc.) and carbon materials (graphite, coke, organic baked substance, etc.) can be mentioned, however since the application of the present invention is meaningful as long

as the hardness of the active material is lower than that of the current collector, the active material is not particularly limited to them.

[0010] The present invention pertains to an improvement of the negative electrode. Therefore, as other members constituting the battery such as positive electrode, nonaqueous electrolyte, and separator, conventional or current practical various members proposed for the secondary lithium battery can be used.

[0011] For example, as active materials of the positive electrode, metal chalcogenide such as TiS_2, MoS_2, and $NbSe_3$; metal oxide such as Cr_2O_5 and V_2O_5; and lithium-transition metal composite oxide such as Li_xMO_z (M is at least one kind of transition element selected from Co, Ni, V, Fe, and Mn, $0 < x \leq 1.3$, $1.8 \leq z \leq 2.2$) can be used.

[0012] Also, as the nonaqueous electrolyte, solvents with a high dielectric constant such as ethylene carbonate, vinylene carbonate, and propylene carbonate, substances in which a /3 solute such as LiPF6 and LiBF4 is dissolved in a mixed solvent of these solvents with a high dielectric constant and solvents with a low boiling point such as diethyl carbonate, dimethyl carbonate, 1,2-dimethoxyethane, 1,2-diethoxytethane, and ethoxymethoxyethane can be used. Also, in addition to the

liquid electrolyte, a solid electrolyte or a gel-state electrolyte (pseudo-solid electrolyte) can also be used.

[0013]

(Operation)

Since the hardness of the additive powder being included in the active material layer formed by pressing the slurry or paste on the current collector is higher than that of the current collector, it is partially sunk into the current collector, so that the contact area of the active material layer and the current collector is increased. As a result, since the adhesion of the active material layer and the current collector is improved, the active material is difficult to drop from the current collector.

[0014]

(Application examples)

Next, the present invention is explained in further detail based on application examples, however the present invention is not limited to the following application examples but can be appropriately modified in the range where its essence is not deviated.

[0015] Application Examples 1-6

Manufacture of positive electrode: $LiNiO_2$ as an active material, acetylene black as an electric conductor, and vinylidene

polyfluoride as a binder were mixed at a weight ratio of 95:2:3, so that a positive electrode mixture was prepared. A slurry was prepared by dispersing the positive electrode mixture into N-methyl-2-pyrrolidone, and the slurry was spread on an aluminum foil, rolled, punched in a disc shape with a diameter of 20 mm, and heat-treated at 150°C for 2 h, so that a positive electrode was manufactured.

[0016] Manufacture of negative electrode: Graphite as an active material, vinylidene polyfluoride as a binder, and Al_2O_3 (mohs hardness 9) with an average particle diameter of 3 μm as an additive powder were mixed at a weight ratio of 95:5:0.01, 95:5:0.05, 95:5:1, 95:5:10, 95:5:20, or 95:5:30, so that negative electrode mixtures were prepared. Slurries were prepared by dispersing each negative electrode mixture into N-methyl-2-pyrrolidone, and these slurries were spread on a copper foil as a current collector, rolled, punched in a disc shape with a diameter of 20 mm, and heat-treated at 150°C for 2 h, so that six kinds of negative electrodes were manufactured. Also, the thickness of the active materials of the negative electrodes was set to 150 μm (active material layers of negative electrodes with the same thickness were also formed in the following application examples and comparative examples).

[0017] Manufacture of nonaqueous electrolyte: Lithium perchlorate ($LiClO_4$) was dissolved at a ratio of 1 M (mole/l) in a mixed solvent of propylene carbonate and 1,2-dimethoxyethane at a volume ratio of 1:1, so that a nonaqueous electrolyte was prepared.

[0018] Assembly of battery: Using the above positive electrode, negative electrodes (six kinds of negative electrodes), and nonaqueous electrolyte, batteries A1-A6 of the present invention (flat secondary lithium batteries) were assembled (battery size: 24.0 mm in diameter and 3.0 mm in thickness). Also, as a separator, a fine porous membrane made of polypropylene was used, and it was impregnated with the above nonaqueous electrolyte.

[0019] Application Example 7

Similarly to Application Examples 1-6 except for using a negative electrode mixture of graphite, vinylidene polyfluoride, and diamond powder (mohs hardness 10) with an average particle diameter of 3 µm at a weight ratio of 95:5:1 in the manufacture of the negative electrode, a battery A7 of the present invention was assembled.

[0020] Application Example 8

Similarly to Application Examples 1-6 except for using a negative electrode mixture of graphite, vinylidene polyfluoride,

and boron nitride (the mohs hardness was confirmed as 4.5 or more from the comparison with iron)at a weight ratio of 95:5:1 in the manufacture of the negative electrode, a battery A8 of the present invention was assembled.

[0021] Application Example 9

Similarly to Application Examples 1-6 except for using a negative electrode mixture of graphite, vinylidene polyfluoride, and boron carbide (the mohs hardness was confirmed as 4.5 or more from the comparison with iron)at a weight ratio of 95:5:1 in the manufacture of the negative electrode, a battery A9 of the present invention was assembled.

[0022] Application Example 10

Similarly to Application Examples 1-6 except for using a negative electrode mixture of graphite, vinylidene polyfluoride, and titanium carbide (the mohs hardness was confirmed as 4.5 or more from the comparison with iron)at a weight ratio of 95:5:1 in the manufacture of the negative electrode, a battery A10 of the present invention was assembled.

[0023] Comparative example

Similarly to Application Examples 1-6 except for using a negative electrode mixture of graphite and vinylidene polyfluoride at a weight ratio of 95:5:1 in the manufacture of the negative electrode, a comparative battery B was assembled.

[0024] Charge and discharge cycle test: Each battery was subjected to a charge and discharge cycle test in which a process of charging at 1 mA up to 4.5 V and discharging at 3 mA up to 2.0 V was one cycle, and the capacity retention rate after 100 cycles (capacity retention rate (%) = (discharge capacity after 100 cycles/discharge capacity after 1 cycle) x 100) was attained. The results are shown in Table I.

[0025]

(Table I)

part by weight · capacity retention

5 · 6

1. 電池	2. 正極の活物質	3. 負極の活物質	4. 添加剤粉末	5. 添加剤粉末の負極への添加量(重量部)	6. 100サイクル目の容量維持率(%)
A 1	$LiNiO_2$	黒鉛	Al_2O_3 粉	0.01	90
A 2	$LiNiO_2$	黒鉛	Al_2O_3 粉	0.05	95
A 3	$LiNiO_2$	黒鉛	Al_2O_3 粉	1	95
A 4	$LiNiO_2$	黒鉛	Al_2O_3 粉 8.	10	95
A 5	$LiNiO_2$	黒鉛	Al_2O_3 粉	20	95
A 6	$LiNiO_2$	黒鉛	Al_2O_3 粉	30	95
A 7	$LiNiO_2$	黒鉛	ダイヤモンド粉 9.	1	95
A 8	$LiNiO_2$	黒鉛	BN粉 10	1	96
A 9	$LiNiO_2$	黒鉛	B_4C 粉 11	1	97
A 10	$LiNiO_2$	黒鉛	TiC 粉 12.	1	96
B	$LiNiO_2$	黒鉛	—	—	80

7. (column)

1. Battery
2. Active material of positive electrode
3. Active material of negative electrode
4. Additive powder
5. amount of additive powder added to the negative electrodes (part by weight)
6. Capacity retention rate after 100 cycles (%)
7. Graphite
8. Al_2O_3 powder
9. Diamond powder
10. BN powder
11. B_4C powder
12. TiC powder

[0026] As shown in Table I, in the batteries A1-A10 of the present invention, the capacity retention rate is high, compared with the comparative battery B. From the fact, it is understood that the charge and discharge cycle characteristics of the conventional secondary lithium battery (the comparative battery B corresponds to it), in which the charge and discharge cycle characteristics were not good due to an easy drop of the active material from the current collector, can be improved by including the additive powder with a hardness higher than that

of the current collector in the active material layer of the negative electrode.

[0027]

(Effects of the invention)

Since the adhesion of the active material layer in the negative electrode and the current collector is good, the active material of the negative electrode is difficult to be separated from the current collector during the charge and discharge cycles. For this reason, the battery of the present invention is excellent in the charge and discharge cycle characteristics.